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fac-Re(CO)$_3$L Complexes Containing Tridentate Monoanionic Ligands (L$^-$) with a Seldom-Studied Sulfonamido Group As One Terminal Ligating Group

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To achieve a net-neutral coordination unit in radiopharmaceuticals with a *fac*-M(CO)$_3^+$ core (M = Tc, Re), facially coordinated monoanionic tridentate ligands are needed. New neutral *fac*-Re(CO)$_3$**L** complexes were obtained by treating *fac*-[Re(CO)$_3$(H$_2$O)$_3$]$^+$ with unsymmetrical tridentate NNN donor ligands (**LH**) based primarily on a diethylenetriamine (dien) moiety with an aromatic group linked to a terminal nitrogen through a sulfonamide. **LH**s contain 2,4,6-trimethylbenzenesulfonyl (tmbSO$_2$) and 5-(dimethylamino)naphthalene-1-sulfonyl (DNS) groups. X-ray crystallographic and NMR analyses confirm that in both the solid and the solution states all **L**$^-$ in *fac*-Re(CO)$_3$**L** complexes are bound in a tridentate fashion with one donor being nitrogen from a deprotonated sulfonamido group. Another fundamental property that is important in radiopharmaceuticals is shape, which in turn depends on ring pucker. For **L**$^-$ = tmbSO$_2$-dien$^-$, tmbSO$_2$-*N*′-Medien$^-$, and tmbSO$_2$-*N*,*N*-Me$_2$dien$^-$, the two chelate rings have a different pucker chirality, as is commonly found for a broad range of metal complexes. However, for *fac*-Re(CO)$_3$(DNS-dien), both chelate rings have the same pucker chirality because the sulfonamido ring has an unusual pucker for the absolute configuration at Re; a finding that is attributable to intramolecular and intermolecular hydrogen bonds from the sulfonamido oxygens to the NH$_2$ groups. Averaging of tmb NMR signals, even at –90 °C for Re(CO)$_3$(tmbSO$_2$-*N*,*N*-Me$_2$dien), indicates rapid dynamic motion in the complexes with this group. However, examination of the structures suggests that free rotation about the S–C(tmb) bond is not possible but that concerted coupled rotations about the N–S and the S–C bonds can explain the NMR data.

Introduction

Metal nuclide radiopharmaceuticals contain a metal core and an inner ligating unit, usually having chelate rings. We refer to this part of the agent as a label, and the important properties of the label, which influence biological behavior, are the charge and overall shape. Technetium-99m (^{99m}Tc) is the most widely used diagnostic radionuclide in nuclear medicine.[1−4] {^{99m}Tc(V)O}$^{3+}$ has been the metal core used most predominantly, but recently the development of the advantageous [^{99m}Tc(CO)$_3$(H$_2$O)$_3$]$^+$ precursor has opened new directions for radiolabeling.[5−7] Schibli et al. showed that agents with the *fac*-^{99m}Tc(I)(CO)$_3^+$ core bearing a tridentate-coordinated ligand are more robust and have better pharmacokinetic profiles than agents bearing bidentate ligands.[8] Commonly employed chelating ligands (e.g., diethylenetriamine (dien),[9] cysteine-based ligands, and homocysteine-based ligands[10,11]) contain nitrogen, oxygen, or sulfur donor atoms in groups such as carboxyls,[12] amines,[13−19] nitrogen heterocycles,[14−16] and thioethers.[10,11,16,17]

An important approach in the development of small (∼5 kDa) metal nuclide radiopharmaceuticals is the bioconjuga-

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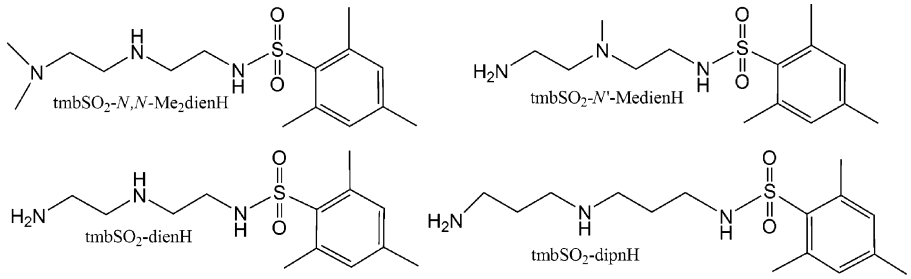

Figure 1. Ligands used in this study: *N*-[2-(2-dimethylaminoethylamino)-ethyl]-2,4,6-trimethylbenzenesulfonamide (tmbSO$_2$-*N*,*N*-Me$_2$dienH); *N*-{2-[(2-aminoethyl)-methylamino]-ethyl}-2,4,6-trimethylbenzenesulfonamide (tmbSO$_2$-*N*′-MedienH); *N*-[2-(2-aminoethylamino)-ethyl]-2,4,6-trimethylbenzenesulfonamide (tmbSO$_2$-dienH); and *N*-[3-(3-aminopropylamino)-propyl]-2,4,6-trimethylbenzenesulfonamide (tmbSO$_2$-dipnH).

tion of a net-neutral label to hormones, small peptides, etc.[20] For *fac*-^{99m}Tc(I)(CO)$_3^+$ agents, the ligand(s) occupying the three remaining coordination sites must have one negative group close to the metal, for net neutrality. A coordinated carboxylate group provides such a unit, but it does not provide a point for ligand elaboration or for bioconjugation. Consequently, there is a need to evaluate other groups within tridentate monoanionic ligands. In this study, we explore ligands that provide one metal-bound negative group and offer a diverse chemistry, allowing bioconjugation via internal ligand atoms or via a seldom-used negative terminal ligating group.[21] We use ligands containing the sulfonamide group, which has been shown to bind well to several metals,[22−29] but Tc complexes with this group have not been studied.

The nonradioactive *fac*-[Re(CO)$_3$(H$_2$O)$_3$]$^+$ analogue is useful in understanding the chemistry of agents derived from the [^{99m}Tc(CO)$_3$(H$_2$O)$_3$]$^+$ species.[10] As a prelude to radiopharmaceutical studies, we analyzed a series of new Re(CO)$_3$**L** complexes formed by treating [*fac*-Re(CO)$_3$(H$_2$O)$_3$]$^+$ with four new ligands, **LH**, bearing a sulfonamide group (Figure 1). These ligands, tmbSO$_2$-*N*,*N*-Me$_2$dienH, tmbSO$_2$-*N*′-MedienH, tmbSO$_2$-dienH, and tmbSO$_2$-dipnH, bind in a tridentate fashion involving one nitrogen of a monoanionic deprotonated sulfonamido group. The hydrogens in the ligand names (cf. the caption of Figure 1) designate the sulfonamide NH proton that is absent in the deprotonated bound ligand. We provide the first detailed analysis of X-ray structures with a sulfonamido group bound to Re.

Given the promise of the ^{99m}Tc(CO)$_3$**L** agents (**L**$^-$ = a facially coordinated tridentate ligand), it is clearly important to understand how the ligand pucker depends on the various components that can influence it (donor atoms, chains linking these atoms, exocyclic substituents, etc.). Because the chelate-ring atoms act as a fulcrum, the configuration of asymmetric centers, the shape, and the conformation of the rings can have a large effect on the overall shape of the agent and, hence, on its biological activity.

Although chelate-ring pucker and factors affecting pucker have not been thoroughly examined for radiopharmaceuticals, extensive structural information exists for a large number of complexes with other metals containing chelate rings with an ethylene group bridge between ligating atoms. Many of these structures have been analyzed using principal component analysis (pca) and other methods.[30−37] When diethylenetriamine-type ligands bind to a metal center in a tridentate fashion, the pucker of the two five-membered chelate rings can have either δ or λ chirality (Chart 1), leading to four possible combinations of chelate-ring chirality: $\delta\lambda$, $\lambda\delta$, $\lambda\lambda$, and $\delta\delta$.

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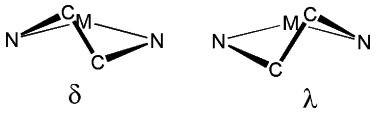
Chart 1



In pca studies of X-ray structures from the Cambridge Structural Database (CSD) of $[M(dien)_2]^{n+}$ (M = Ni, Co, Zn, Cu, Cr, Rh, and Ir)[31] and of $[M(dien)L_n]$[32] complexes and M(dien) fragments,[30] the $\delta\lambda$ and $\lambda\delta$ conformation combinations were found much more frequently than combinations with the same pucker chirality ($\delta\delta$ and $\lambda\lambda$). On the other hand, Schmidtke and Garthoff[33] suggested that, because of steric effects of the hydrogen atoms of the ethylene chains, *fac* coordination would favor a $\delta\delta$ or $\lambda\lambda$ combination. Thus, factors influencing pucker (which in turn affect shape) are not well understood, and in a recent study, we found that the rings have the same pucker in complexes of lanthionine ($LANH_2$).[11] The new $Re(CO)_3$**L** complexes studied here offer the opportunity to determine how widespread is the occurrence of $\delta\lambda$ and $\lambda\lambda$ combinations.

Experimental Section

Starting Materials. *N*,*N*-dimethyldiethylenetriamine (*N*,*N*-Me_2-dien) from Ames Laboratories, *N*-methyl-2,2′-diaminodiethylamine (*N*′-Medien) from TCI America, and bis(3-aminopropyl)amine (dipn), dien, 2-mesitylenesulfonyl chloride ($tmbSO_2Cl$), dansyl chloride (DNS−Cl), and $Re_2(CO)_{10}$ from Aldrich were all used as received. The DNS-dienH ligand (*N*-(2-((2-aminoethyl)amino)-ethyl)-5-(dimethylamino)naphthalene-1-sulfonamide)[38] and the $[Re(CO)_3(H_2O)_3]OTf$[10] (OTf = trifluoromethanesulfonate) precursor were prepared by known methods.

Physical Measurements. ^{1}H NMR spectra were recorded on either a 300 MHz or a 400 MHz spectrometer. Peak positions are relative to tetramethylsilane (TMS) or the solvent residual peak with TMS as reference. All of the NMR data were processed with XWINNMR and Mestre-C software. IR spectra were recorded on a Bruker TENSOR 37 spectrometer, and the values for the CO stretching frequencies are given in the Supporting Information.

X-ray Data Collection and Structure Determination. All of the single crystals suitable for X-ray crystallography were obtained by slow evaporation from acetone or methanol. Single crystals were placed in a cooled nitrogen gas stream at ∼100 K on a Nonius Kappa CCD diffractometer fitted with an Oxford Cryostream cooler with graphite-monochromated Mo Kα (0.71073 Å) radiation. Data reduction included absorption corrections by the multiscan method, with HKL SCALEPACK.[39] All of the X-ray structures were determined by direct methods and difference Fourier techniques and refined by full-matrix least-squares techniques, using SHELXL97.[40] All of the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were visible in difference maps, but were placed in idealized positions. One methyl group (C17) of **5** has its hydrogen atoms disordered into a doughnut of electron density, which was modeled as six half-populated positions. A torsional parameter was refined for each methyl group. and Mercury Software was used as an aid for measuring structural parameters.

Synthesis of $Re(CO)_3$L. The crude ligands, **LH**, were synthesized by a slight modification of the method of Krapcho and Kuell.[41] A solution of the sulfonyl ($tmbSO_2Cl$) or acetyl chloride (tmbCOCl) (∼5 mmol, 100 mL of dioxane) was added dropwise over the course of about 2 h to a solution of the amine (∼50 mmol, 100 mL of dioxane). The reaction mixture was stirred at room temperature for 10 h. The dioxane was completely removed under a vacuum, and water (50 mL) was added. The product was extracted into CH_2Cl_2 (2 × 100 mL), and the solvent was removed under rotary evaporation. The oil thus obtained was used to synthesize the $Re(CO)_3$**L** complexes as follows: an aqueous solution of $[Re(CO)_3(H_2O)_3]^+$ (10 mL, 0.1 mmol) was treated with a methanol (1 mL) solution of the ligand (0.1 mmol). The pH was adjusted to ∼5, and the reaction mixture was heated at reflux for 10 h and then allowed to cool at room temperature, and the pH was increased to ∼7. The resulting white solid that precipitated was collected on a filter, washed with water, and dried under a vacuum.

$Re(CO)_3$(tmbSO$_2$-*N*,*N*-Me$_2$dien) (1). The general method just described, with $tmbSO_2Cl$ (1 g) and *N*,*N*-Me_2dien (6.5 mL), yielded the crude $tmbSO_2$-*N*,*N*-Me$_2$dienH ligand (750 mg, 51% yield). ^{1}H NMR (ppm) in $CDCl_3$: 6.94 (s, 2H), 2.90 (t, 2H, CH_2), 2.66 (t, 2H, CH_2), 2.64 (s, 6H, CH_3), 2.55 (t, 2H, CH_2), 2.33 (t, 2H, CH_2), 2.29 (s, 3H, CH_3), 2.20 (s, 6H, NCH_3). Treatment of $[Re(CO)_3(H_2O)_3]^+$ (0.1 mmol) with $tmbSO_2$-*N*,*N*-Me$_2$dienH (32 mg) as described above afforded $Re(CO)_3$($tmbSO_2$-*N*,*N*-Me$_2$dien) as a white powder (26 mg, 44% yield). Crystals obtained by slow evaporation from methanol were characterized by single-crystal X-ray crystallography. ^{1}H NMR (ppm) spectrum in acetone-d_6: 6.91 (s, 2H), 6.17 (b, 1H, N2H), 3.54−3.10 (m, 6H, CH_2), 3.10 (s, 6H, N−CH_3), 2.70 (s, 6H, CH_3), 2.59 (m, 2H, CH_2), 2.24 (s, 3H, CH_3).

$Re(CO)_3$(tmbSO$_2$-*N*′-Medien) (2). The general method, with $tmbSO_2Cl$ (1 g) and *N*′-Medien (6 mL), afforded the crude $tmbSO_2$-*N*′-MedienH ligand (650 mg, 48% yield). ^{1}H NMR (ppm) in $CDCl_3$: 6.95 (s, 2H), 2.93 (t, 2H, CH_2), 2.75 (t, 2H, CH_2), 2.64 (s, 6H, CH_3), 2.44 (t, 2H, CH_2), 2.38 (t, 2H, CH_2), 2.29 (s, 3H, CH_3), 2.08 (s, 3H, N′-CH_3). Treatment of $[Re(CO)_3(H_2O)_3]^+$ (0.1 mmol) with $tmbSO_2$-*N*′-MedienH (30 mg) as described above afforded $Re(CO)_3$($tmbSO_2$-*N*′-Medien) as a white powder (24 mg, 42% yield). Crystals obtained by slow evaporation from acetone were characterized by single-crystal X-ray crystallography. ^{1}H NMR (ppm) spectrum in acetone-d_6: 6.91 (s, 2H), 4.94 (b, 1H, N1H), 3.87 (b, 1H, N1H), 3.42−3.53 (m, 3H, CH_2), 3.24 (s, 3H, N′-CH_3), 3.01−3.18 (m, 5H, CH_2), 2.64 (s, 6H, CH_3), 2.24 (s, 3H, CH_3).

$Re(CO)_3$(tmbSO$_2$-dien) (3). The general method, with $tmbSO_2$-Cl (1 g) and dien (5.2 mL), yielded the crude $tmbSO_2$-dienH ligand (600 mg, 54% yield). ^{1}H NMR (ppm) in $CDCl_3$: 6.93 (s, 2H), 2.92 (t, 2H, CH_2), 2.73 (t, 2H, CH_2), 2.67 (t, 2H, CH_2), 2.63 (s, 6H, CH_3), 2.59 (t, 2H, CH_2), 2.28 (s, 3H, CH_3). Treatment of $[Re(CO)_3(H_2O)_3]^+$ (0.1 mmol) with $tmbSO_2$-dienH (31.2 mg) as described above afforded $Re(CO)_3$($tmbSO_2$-dien) as a white powder (21 mg, 38% yield). Crystals obtained by slow evaporation from methanol were characterized by single-crystal X-ray crystallography. ^{1}H NMR (ppm) spectrum in acetone-d_6: 6.90 (s, 2H), 6.17 (b, 1H, N2H), 4.75 (b, 1H, N1H), 3.98 (b, 1H, N1H), 3.36−3.00 (m, 8H, CH_2), 2.65 (s, 6H, CH_3), 2.24 (s, 3H, CH_3).

$Re(CO)_3$(tmbSO$_2$-dipn) (5). The general method, with $tmbSO_2$-Cl (1 g) and dipn (6 mL), produced the crude $tmbSO_2$-dipnH ligand (600 mg, 42% yield). ^{1}H NMR (ppm) in $CDCl_3$: 6.94 (s, 2H), 2.98 (t, 2H, CH_2), 2.76 (t, 2H, CH_2), 2.71 (t, 2H, CH_2), 2.63 (t, 2H, CH_2), 2.63 (s, 6H, CH_3), 2.29 (s, 3H, CH_3), 1.62 (m, 4H, CH_2). Treatment of $[Re(CO)_3(H_2O)_3]^+$ (0.1 mmol) with $tmbSO_2$-dipnH (32 mg) as described above afforded $Re(CO)_3$($tmbSO_2$-dipn) as a

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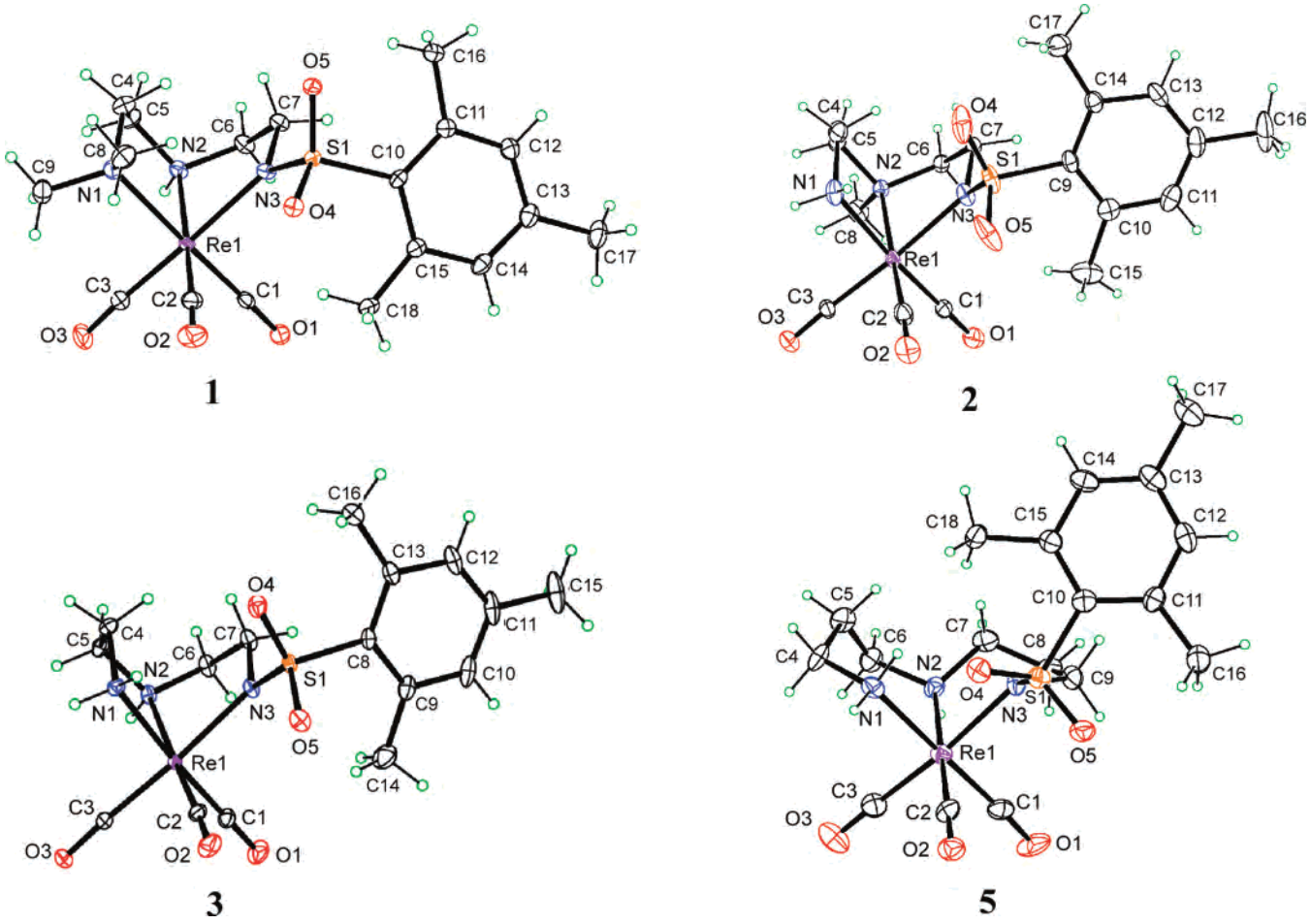

Figure 2. Perspective drawings of the S configuration of $Re(CO)_3(tmbSO_2$-*N*,*N*-Me_2dien) (**1**), $Re(CO)_3(tmbSO_2$-*N*′-Medien) (**2**), $Re(CO)_3(tmbSO_2$-dien) (**3**), and $Re(CO)_3(tmbSO_2$-dipn) (**5**). Thermal ellipsoids are drawn with 50% probability.

Table 1. Crystal Data and Structural Refinement for $Re(CO)_3$**L** Complexes in which $\mathbf{L}^-$ Contains a Sulfonamido Group

	$Re(CO)_3$**L** complex			
	1	**2**	**3**	**5**
empirical formula	$C_{18}H_{26}N_3O_5ReS$	$C_{17}H_{24}N_3O_5ReS{\cdot}0.5H_2O$	$C_{16}H_{22}N_3O_5ReS{\cdot}0.5CH_3OH$	$C_{18}H_{26}N_3O_5ReS$
fw	582.68	577.66	570.65	582.68
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	*C*2/*c*	*P*2/*c*	$P\bar{1}$	$P\bar{1}$
	Unit Cell Dimensions			
a (Å)	38.994(2)	15.945(2)	7.6603(5)	7.956(3)
b (Å)	14.7085(10)	10.9504(15)	7.8808(5)	11.833(4)
c (Å)	14.6254(10)	12.2394(16)	16.6154(12)	12.129(4)
α (deg)	90.0	90.0	98.181(4)	115.71(2)
β (deg)	94.642(4)	100.451(7)	95.974(4)	94.66(2)
γ (deg)	90.0	90.0	98.736(4)	98.50(2)
V, Å^3	8360.8(9)	2101.6(5)	973.20(11)	1003.9(6)
T, K	90	115	90	115
Z	16	4	2	2
ρ_{calc} (g/cm^3)	1.852	1.826	1.947	1.928
abs coeff (mm^{-1})	5.947	5.916	6.386	6.191
$2\theta_{max}$ (deg)	71.2	68.4	82.2	52
R indices[a]	0.028	0.039	0.025	0.045
wR2 = $[I > 2\sigma(I)]$[b]	0.063	0.095	0.069	0.091
data/params	19 029/516	7997/253	12 822/257	3910/255

[a] $R = (\sum||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

white powder (24 mg, 41% yield). Crystals obtained by slow evaporation from acetone were characterized by single-crystal X-ray crystallography. ^{1}H NMR (ppm) spectrum in acetone-d_6: 6.93 (s, 2H), 5.20 (b, 1H, N2H), 4.64 (b, 1H, N1H), 3.98 (b, 1H, N1H), 3.46 (m, 2H, CH_2), 3.28 (s, 2H, CH_2), 3.10−3.19 (m, 3H, CH_2), 3.94 (s, 2H, CH_2), 2.66 (s, 6H, CH_3), 2.25 (s, 3H, CH_3), 1.90 (s, 2H, CH_2), 1.66−1.75 (s, 2H, CH_2).

Results and Discussion

In a modification of the method of Krapcho and Kuell,[41] the monoaddition of the relatively large hydrophobic aromatic $tmbSO_2$ group to triamines produced hydrophobic ligands that were readily extracted into CH_2Cl_2 from water (with an excess of unchanged triamine remaining in the water layer). This method afforded a series of triamine ligand derivatives (**LH**) in sufficient yield and purity for use in preparing rhenium complexes. These ligand derivatives bind to the *fac*-Re(I)$(CO)_3$ center as tridentate deprotonated monoanionic ligands $\mathbf{L}^-$, thereby forming complexes with a neutral core.

X-ray Characterization. Crystal data and structural refinement details are summarized in Table 1 for new complexes and in the Supporting Information (Table S1) for the previously briefly described compound $Re(CO)_3$(DNS-dien), **4**.[42] All of the complexes reported here have a distorted octahedral structure, with the three carbonyl ligands coordinated facially (Figure 2). The remaining coordination sites

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Table 2. Selected Bonded and Nonbonded Distances (Angstroms) and Bond Angles (Degrees) for $Re(CO)_3(tmbSO_2$-*N*,*N*-Me_2dien) (**1**), $Re(CO)_3(tmbSO_2$-*N*′-Medien) (**2**), $Re(CO)_3(tmbSO_2$-dien) (**3**), $Re(CO)_3$(DNS-dien) (**4**), and $Re(CO)_3(tmbSO_2$-dipn) (**5**)

	$Re(CO)_3$**L** complex				
	1	**2**	**3**	**4**	**5**
		Bond Distances			
Re−N1	2.2873(19)/2.2880(19)	2.222(4)	2.2247(15)	2.204(3)	2.209(7)
Re−N2	2.2065(19)/2.2156(18)	2.232(3)	2.2172(15)	2.222(3)	2.249(7)
Re−N3	2.2022(18)/2.2007(17)	2.195(3)	2.1898(15)	2.166(3)	2.197(6)
		Bond Angles			
N1−Re−N2	78.87(7)/78.15(7)	78.79(13)	78.24(6)	77.48(11)	86.4(2)
N2−Re−N3	75.89(7)/75.45(7)	76.62(12)	75.96(5)	74.42(12)	81.5(2)
N1−Re−N3	86.79(7)/86.75(7)	84.06(14)	84.06(6)	82.77(12)	84.7(2)
N2−Re−C2	171.57(9)/172.02(8)	173.97(18)	171.58(7)	171.86(13)	178.8(3)
		Nonbonded Distances			
N1 to N2	2.855/2.839	2.826	2.803	2.769	3.051
N2 to N3	2.711/2.702	2.702	2.745	2.653	2.903
C4 to C7	3.258/3.234	3.169	3.206	3.907	
C4H to C7H	2.156/2.112	1.991	2.027	3.927	
C5 to C6	2.496/2.497	2.494	2.509	2.494	
C5H to C6H	2.256/2.269	2.289	2.291	2.361	

are occupied by two sp^3 nitrogen amines and one sp^2 nitrogen from a sulfonamido group. Typically, the Re−C(3) bond distances, involving the CO group trans to the sulfonamido group, are not significantly different from those of the other Re−CO bonds.

Although we found that the aromatic rings facilitated our efforts to obtain crystals, these rings generally were not stacked. The closest distance between carbons of two benzene rings (3.69 Å) was found for $Re(CO)_3(tmbSO_2$-*N*,*N*-Me_2dien) (**1**), in which the two carbons were in the two slightly different molecules of the asymmetric unit. This distance of 3.69 Å is too long to indicate stacking interactions between the aromatic rings.

(a) Bond Lengths and Hybridization. The average Re−N bond length of ∼2.2 Å (Table 2 for selected bond lengths and angles of the sulfonamido complexes) found in the sulfonamido complexes is consistent with distances found in relevant $Re(CO)_3$ complexes containing dien, such as [$Re(CO)_3$(dien)]Br.[9] The ∼0.2 Å longer Re−N bonds in $Re(CO)_3$**L** compared to relevant Pt−N bonds (e.g., including terminal amines, 2.063(9) and 2.063(10) Å, and the secondary amine, 2.002(8) Å, of [Pt(dien)Cl]Cl[43]) are explained by the greater radius for Re(I). The Re−N1 bond (to the terminal amine) in $Re(CO)_3(tmbSO_2$-*N*,*N*-Me_2dien) (**1**) is significantly longer than the other Re−N bonds in **1** and the other sulfonamido compounds **2**−**5**. This lengthening is attributed to the bulkiness of the two methyl groups on N1 (for **1**) compared to the smaller H group in all of the other sulfonamido compounds.

The sp^2 nitrogen donors can form shorter Re−N bonds than can the sp^3 nitrogen donors.[14,44] Typical Re-sp^2 nitrogen bond lengths range from 2.14 to 2.18 Å, as measured in a number of rhenium structures containing Re−N bonds (aromatic sp^2 N, e.g. in pyridyl ligands), whereas a typical Re-sp^3 nitrogen bond length is ∼2.2 Å.[10,11,14] The sp^2-hybridized N3 should affect the S−N3−C7, S−N3−Re, and C7−N3−Re angles. However, although we have several structures to compare, the differences between molecules were generally consistent with expectations for Re-sp^2 nitrogen versus Re-sp^3 nitrogen centers; these differences are small and thus are masked by steric and solid-state effects.

The $N-SO_2$ bond lengths for the deprotonated sulfonamido group, between 1.561(3)−1.5902(18) Å for complexes **1** to **5**, are within the relatively broad range for $N-SO_2$ bonds (1.5−1.7 Å) found in deprotonated sulfonamides bound to a metal (e.g., Cu, Zn, and Ni).[22,24]

(b) Bite Angles. The N1 to N2 and N2 to N3 distances within five-membered chelate rings in the $Re(CO)_3$**L** complexes have a narrow range of values (Table 2). The distances of about 2.7 Å are similar to relevant distances in complexes with higher-valent metal centers (e.g., rhenium(V) and platinum(II)) with shorter M−N bonds (∼2 Å) (e.g. in [Pt(dien)Cl]Cl, the N to N distances average about 2.72 Å).[43] The combination of the long Re−N bonds (compared to other M−N bonds) and typical N to N distances results in more acute values for N−Re−N chelate-ring bite angles (less than 90°) and for trans N−Re−C angles (less than 180°) (Table 2). For complexes with five-membered rings (**1**−**4**), the N2−Re−N3 bite angle (N3 is part of the sulfonamido group) is smaller (74.42−76.62°) than the N1−Re−N2 bite angle (77.5−78.9°). These values are significantly smaller than the respective bite angles, 81.5° and 86.4°, in $Re(CO)_3(tmbSO_2$-dipn) (**5**), as expected from the large six-membered rings in this complex. Nevertheless, these angles for **5** are less than that (∼89.5°) for $Re(CO)_3$(*N*,*N*,*N*′,*N*′-tetramethyl-1,3-propylenediamine)Br.[45] Although the methyl groups cause the Re−N bonds to be very long (2.3 Å), the latter complex also has a very long N to N distance (3.25 Å), explaining the large bite angle.

(c) Chirality and Conformation of Chelate Rings. For **1**, **2**, and **3**, the pucker of the two chelate rings has different chirality. As mentioned, a different chirality for the pucker of each dien chelate ring is found most often.[30−32] Because the ligands in this study are unsymmetrical, we report chirality combinations by giving the pucker chirality of the ring with the terminal amine, followed by that of the ring with the sulfonamido group. Also, we specify the absolute configuration because the unsymmetrical nature of the ligand creates asymmetric central nitrogen (N2) and rhenium centers. Specifically, this combination for **1**−**3** is $\lambda\delta$ for the enantiomer with the S absolute configuration (determined by the absolute configuration at N2, Figure 3). In contrast, both chelate rings of $Re(CO)_3$(DNS-dien) (**4**) have pucker with the same chirality (both λ for the S configuration). This less-common situation with the same pucker chirality for both rings also occurs in the $Re(CO)_3$(LANH)complexes.[11] The meridionally coordinated ligand in the pseudo-square-planar Pt($tmbSO_2$-*N*,*N*-Me_2dien)Cl complex (work in progress) has the $\delta\lambda$ chirality combination (S absolute configuration at the central nitrogen).

(43) Britten, J. F.; Lock, C. J. L.; Pratt, W. M. C. *Acta Crystallogr., Sect. B* ***1982***, *38*, 2148−2155.
(44) Correia, J. D. G.; Domingos, A.; Santos, I.; Alberto, R.; Ortner, K. *Inorg. Chem.* **2001**, *40*, 5147−5151.
(45) Horn, E.; Onai, S. *Z. Kristallogr.—New Cryst. Struct.* **2001**, *216*, 75−76.

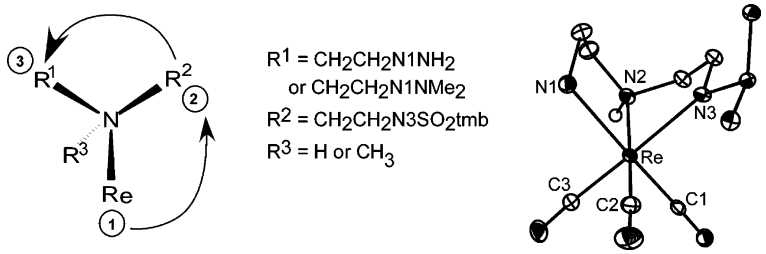

Figure 3. Absolute configuration. When the structure is viewed with the nonchelate ring substituent on N2 projecting away from the viewer (left), the absolute configuration at N2 (left) and rhenium (right) is designated to be S for a counterclockwise trace for the other nitrogen substituents (rhenium, R^1, and R^2) according to higher priority as shown. When the trace is clockwise the absolute configuration is R.

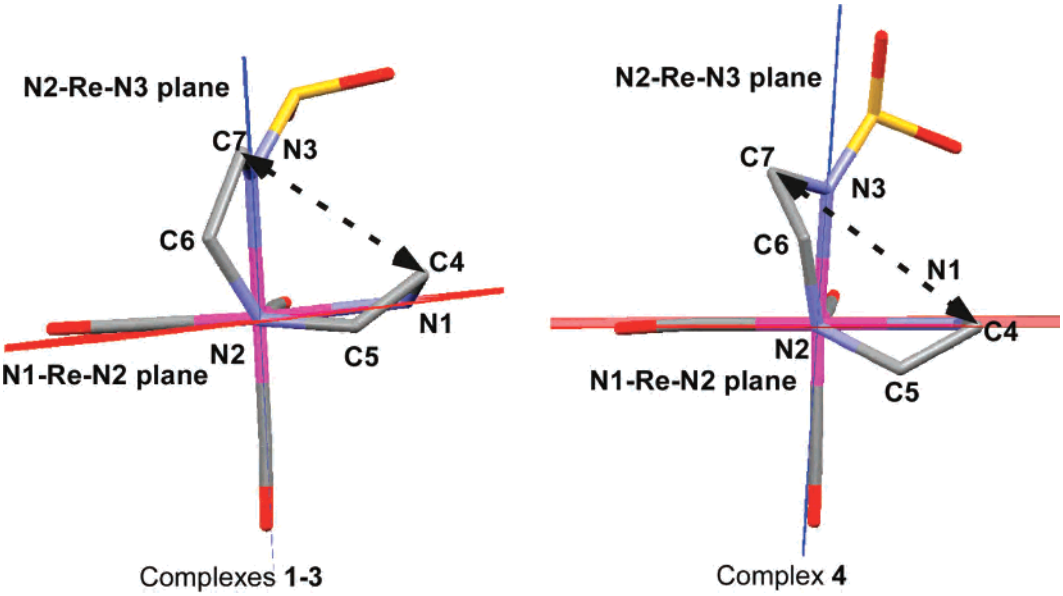

Figure 4. Illustration of the shorter C4 to C7 nonbonded distances for complexes **1**−**3** (different pucker chirality) compared to complex **4** (same pucker chirality). Note the similarity of the C5 to C6 nonbonded distances. Also shown are the positions of the C4 and C5 atoms relative to the N1−Re−N2 plane (red line) and the C6 and C7 atoms relative to the N2−Re−N3 (blue line) plane.

In an early study based on IR data, Schmidtke and Garthoff[33] determined that the $\delta\delta$ or $\lambda\lambda$ combination was the most favorable for facial coordination of diethylenetriamine in complexes of several metals (Cr, Co, Rh) and proposed that steric effects of the hydrogens of the ethylene chain would also favor the $\delta\delta$ or $\lambda\lambda$ combination. We compared selected nonbonded distances for **1**−**4** (Table 2) involving chelate-ring carbons and hydrogens on these carbons projecting toward the center of the triangular face occupied by $\mathbf{L}^-$. Whether the pucker chirality of the two chelate rings in a given complex is the same or different, the C5 to C6 (Figure 4) and C5H to C6H distances are not very different. In contrast, when the chirality of the two chelate rings is the same, the C4 to C7 (Figure 4) and C4H to C7H distances are larger than when the chirality is different. For example, the C4 to C7 distance for **4** (same chirality) is 3.9 Å, whereas the respective distance for complexes **1**−**3** (different chirality) is ∼2 Å.

It is obvious from Figure 4 that the distance from C4 to C7 is much larger when the pucker chirality is the same in both rings, as it is in complex **4**, compared to when the chirality is different, as it is in complexes **1**−**3**. Our observations appear to support the early suggestion of Schmidtke and Garthoff,[33] and the $\delta\delta$ and $\lambda\lambda$ combinations should be favored. However, later literature surveys[31,32] find that X-ray structures of complexes more frequently have different chirality in the two rings. In particular, one pca study on X-ray structures from the Cambridge Structural Database (CSD) showed that 74 fragments had the $\delta\lambda$ chirality combination, 16 fragments had the $\lambda\delta$ chirality combination, 18 fragments had the $\delta\delta$ chirality combination, and 18 enantiomeric fragments had the $\lambda\lambda$ chirality combination.[30] This study agreed with earlier pca studies.[31,32] This overwhelming evidence for a predominance of structures with different pucker chirality is surprising, given that the distances between hydrogens or carbons on the two rings (Table 2, Figure 4) are clearly shorter than the sum of the van der Waals radii both for carbon (3.4 Å) and for hydrogen (2.4 Å).[46] This proximity leads to steric repulsion between rings, as suggested by Schmidtke and Garthoff.[33] Additional studies are needed to clarify factors influencing pucker, but at this time it seems reasonable to assume in designing radiopharmaceuticals with the $^{99m}Tc(CO)_3$ label that the pucker chirality of the rings will be different.

Solution Behavior. (a) Trimethylbenzyl Group Rotation. In the X-ray structures of the tmb−sulfonamido complexes (**1**, **2**, **3**, and **5**) the 3 and 5 protons and the 2 and 6 methyl groups of the $tmbSO_2$ group are not equivalent.

(46) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

When modeling software is used to rotate the tmb group around the S−C bond, beginning with the solid-state structure of **3**, clashes are observed between the methyl groups and a CH_2 group of the chelate ring. For **3**, the distance from C7 to C16 (of the CH_3 group in position 2) becomes as short as ∼1.9 Å, much less than the sum of the van der Waals radii for two carbons (3.4 Å).[46] The resulting impediment to rotation about the S−C(tmb) bond should lead to well-separated ^{1}H NMR signals. Indeed, in $Re(CO)_3$(tmbCO-dien, (tmbCO-dienH = *N*-[2-(2-aminoethylamino)-ethyl]-2,4,6-trimethylbenzamide, unpublished work), where the tmb is linked through a deprotonated amido group instead of a sulfonamido group, the ^{1}H NMR signals of the 3 and 5 protons and the 2 and 6 methyl groups of the tmbCO group are separate, consistent with the expected slow rotation from a similar comparison using modeling software. However, even at low temperature, these tmb ^{1}H NMR signals are not resolved for the tmb−sulfonamido complexes. (The ^{1}H NMR spectrum of **1** (acetone-d_6) recorded at −90 °C has no significant differences from the one recorded at 25 °C.) Further examination of the possible rotations around the S−C and N3−S bonds in the tmb−sulfonamido complexes reveals that concerted rotations about both of these bonds can allow the tmb group to rotate more freely. In particular, if the N3−S bond is rotated by ∼56°, the tmb group can rotate freely around the S−C(tmb) bond, and the closest distance between C7 and C16 (of the CH_3 group in position 2) is ∼3.2 Å; slight changes in bond angles should increase this distance.

The structures of **1**−**5** indicate considerable conformational freedom around the N−S bond (cf. Figure S2 in the Supporting Information). In contrast, the N−C bond in the relatively planar amido group has more double-bond character than the N−S bond of the sulfonamido group. These features limit the CO group to only two favorable orientations, and in both orientations, serious clashes are observed when the tmb group is rotated around the C−C(tmb) bond. In addition, the sulfonamido group has longer bonds (N−S and S−C) compared to the respective bonds (N−C and C−C) of the amido group in $Re(CO)_3$(tmbCO-dien). Therefore, we believe that synchronous rotations about the longer N−S and S−C bonds can explain the relatively free rotation of the tmb group, especially because the sulfonamide group is known to be in relatively faster rotation than the amide group.[47]

(b) NMR Characterization of $Re(CO)_3$L (L$^-$ = tmbSO$_2$-*N*,*N*-Me$_2$dien$^-$, tmbSO$_2$-*N*′-Medien$^-$, tmbSO$_2$-dien$^-$, DNS-dien$^-$ and tmbSO$_2$-dipn$^-$). The $Re(CO)_3$**L** complexes were characterized by NMR spectroscopy (Table 3) in different solvents (DMSO-d_6 and acetone-d_6). For a given solvent, the shifts of the respective $N1H_2$ and N2H signals were similar in all of the complexes reported here. For complexes **2**−**5** with a terminal amino group, the NH signals of this group have a separation (Δ ppm) of between 1 and 2 ppm in DMSO-d_6. In general, terminal amino groups in platinum complexes have two separate signals with a Δ ppm of between 0.1 and 0.3.[26] Specifically, in DMSO-d_6, the amino groups of **2**−**5** each have one downfield-shifted NH signal with a normal shift between 5.21 and 5.46 ppm, which is comparable to the shifts (5.11−5.66 ppm) of the respective NH signals of the NH_2 group in Pt(DNSH-dien)Cl and [Pt(dien)Cl]Cl.[26] The upfield-shifted NH signal of **2**−**5** is between 3.30 and 3.59 ppm, which is ∼1.5 ppm abnormally upfield compared to the NH signals of platinum(II) complexes.

Table 3. Selected ^{1}H NMR Chemical Shifts (ppm) of $Re(CO)_3$(tmbSO$_2$-*N*,*N*-Me$_2$dien) (**1**), $Re(CO)_3$(tmbSO$_2$-*N*′Medien) (**2**), $Re(CO)_3$(tmbSO$_2$-dien) (**3**), $Re(CO)_3$(DNS-dien) (**4**), and $Re(CO)_3$(tmbSO$_2$-dipn) (**5**)[a]

	$Re(CO)_3$**L** complex				
	1[a]	**2**[a]	**3**	**4**[a]	**5**[a]
			DMSO-d_6		
N1HB/Me	2.96	3.30	3.48	3.59	3.30
N1HA/Me	2.96	5.46	5.22	5.21	5.25
N2H	6.77		6.76	6.79	5.81
			acetone-d_6		
N1HB/Me	3.10	3.87	3.98	4.09	4.00
N1HA/Me	3.11	4.94	4.75	4.77	4.66
N2H	6.17		6.17	6.23	5.20

[a] Assignments of the NH signals of **2**, **4**, and **5** were made by analogy with signals for **3** assigned by COSY spectra.

A ^{1}H−^{1}H COSY experiment for **3** in combination with torsion angles allowed the assignment of the NH signals. (Table S3 in the Supporting Information for X-ray structural data for torsion angles between the protons on N1 and C4). According to the Karplus equation,[48] when the torsion angle between two protons is 90°, no coupling is observed between the two protons (^3J = ∼0 Hz); a maximum ^3J is observed (^3J = ∼9.5 Hz) when the torsion angle is 180°. For $Re(CO)_3$(tmbSO$_2$dien) (**3**), the NH_2 signals are correlated by a COSY cross-peak. Also, the downfield N1H signal is coupled to both C4H signals, whereas the upfield N1H signal is coupled to only one C4H signal. The H1B−N1−C4−H4B torsion angle is ∼80° for **3** (Table S3), predicting a weak N1HB−C4HB COSY cross-peak, whereas the H1A−N1−C4−H4A torsion angle is ∼157° (close to 180°) for **3**, predicting a strong N1HA−C4HA COSY cross-peak (cf. Figure S3 for numbering, in the Supporting Information). The H1B−N1−C4−H4A and H1A−N1−C4−H4B torsion angles are both similar for both compounds, and the N1HB−C4HA and N1HA−C4HB cross-peaks were of similar size. Therefore, the downfield NH_2 signal can be identified as H1A (anti to the sulfonamido group) and the upfield NH_2 signal as H1B. The reasons that the NH1A signal for **2**−**5** has a normal shift and the N1HB signal has an unusually upfield shift are unclear, and further investigation is required.

(c) Reactions of Sulfonamido Complexes. Under neutral conditions (DMSO-d_6/D_2O 250 μL/550 μL, pH = 7.70), no change was observed in the ^{1}H NMR signals of **3**, even after 2 days. When a DMSO-d_6 solution of **3** (3 mM) was made basic (dien, 10 equiv), no change was observed in the ^{1}H NMR signals of **3**, even after the solution was heated at ∼60 °C for 16 h. Thus, **3** is stable under neutral and basic conditions, and a good ligand such as dien did not replace

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the $tmbSO_2$-dien ligand. Within minutes after sulfonamido complex **3** (4 mM) was dissolved under acidic conditions (DMSO-d_6/1 M HNO_3, 600 μL/20 μL, final $[H^+] = 0.3$ M), the ^{1}H NMR spectrum was recorded. The sulfonamide NH signal appeared, (7.53 ppm), the N2H signal shifted upfield (5.65 ppm), and the N1H signals moved downfield (5.41 and 4.08 ppm). Similar results were observed when complex **5** was dissolved in the same acidic conditions; a downfield sulfonamide signal appeared (7.76 ppm), the N2H signal (5.29 ppm) and the N1H signal (5.03 ppm) shifted upfield, and the second N1H signal was under the water signal. These NMR data indicate that the sulfonamido nitrogen dissociates upon protonation, and the ligand is now bound to the *fac*-$Re(CO)_3$ moiety in a bidentate fashion through N1 and N2. Bidentate binding for the DNS-dienH ligand has been reported in the Pt(DNS-dienH)Cl_2 complex.[26] Comparisons of the ^{1}H NMR spectrum for the latter complex to those obtained for **3** and **5** under acidic conditions leave little doubt about the bidentate nature of the products. In these cases, the signal of the central NH is substantially upfield in the bidentate ligand compared to the tridentate ligand. A similar relationship of the NH shifts has been reported for $Re(CO)_3$ complexes of an NNN ligand.[16]

Conclusions

The tridentate monoanionic sulfonamido ligands studied here bind to the *fac*-$Re(CO)_3$ core, giving an inner coordination sphere with a neutral charge. In strongly acidic conditions, the sulfonamido group dissociates with protonation, giving a monocationic inner coordination sphere. The sulfonamido group in these complexes can act as a potential anchor for bioconjugation, indicating that this class of tridentate ligands should be useful in the development of radiopharmaceuticals with a $^{99m}Tc(CO)_3$ label. The dangling group connected through the sulfonamido bond undergoes free rotation on the NMR time scale, even at low temperature. Most complexes reported here have different chirality in each chelate ring, even though less-severe steric clashes are expected when both chelate rings have the same chirality. We find in published and in our ongoing studies that the related amido complexes are much more difficult to synthesize, consistent with the paucity of related amido complexes in the literature. In contrast, the sulfonamido group has somewhat similar chemistry, and more use of this group should be made in coordination chemistry.

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Supporting Information Available: Synthesis details, crystal data, and structural refinement for $Re(CO)_3$(DNS-dien) (**4**). Crystallographic data for $Re(CO)_3$($tmbSO_2$-*N*,*N*-Me_2dien) (**1**), $Re(CO)_3$-($tmbSO_2$-*N*′-Medien) (**2**), $Re(CO)_3$($tmbSO_2$-dien) (**3**), $Re(CO)_3$-(DNS-dien) (**4**), and $Re(CO)_3$($tmbSO_2$-dipn) (**5**) in CIF format. Distances of ethylene chain carbons to the N−Re−N plane, selected torsion angles (deg), IR CO-stretching absorptions for **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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